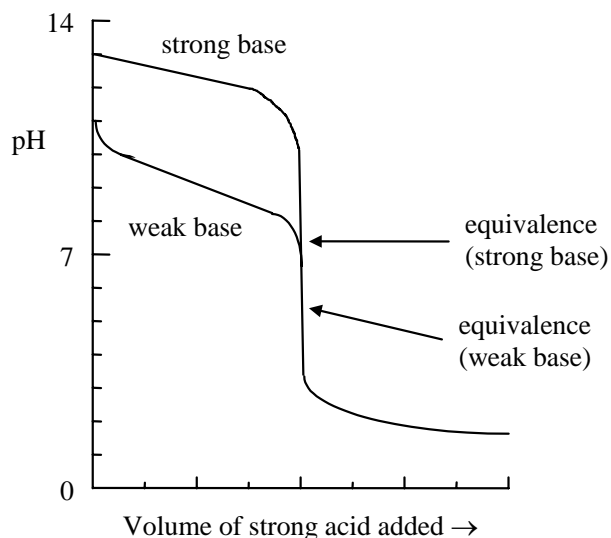


## pH curves and indicators

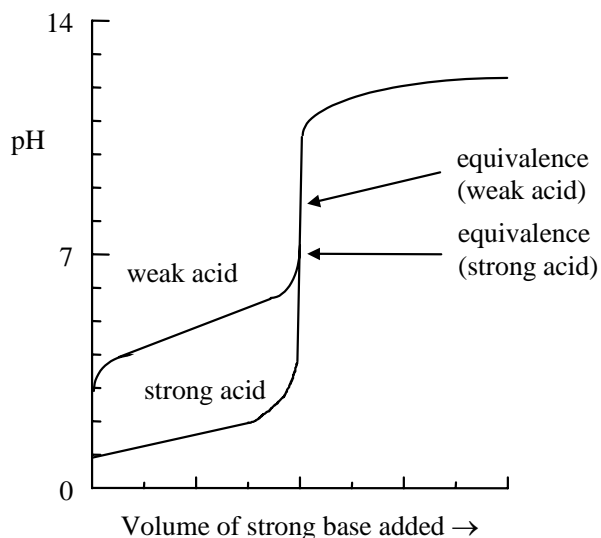
### pH curves

During an acid-base titration, the pH changes in a characteristic way. A **pH curve** is found if the pH of the solution being titrated is plotted against the volume of solution added.

Some typical pH curves in which 0.1M solutions of various acids and bases are titrated together are shown in figures 1 and 2 (below). The  $K_a$  for the weak acid is 4.75 (like ethanoic acid), and the  $K_a$  for the conjugate acid of the weak base is 9.25 (like  $\text{NH}_4^+$ , the conjugate acid of ammonia).



**Figure 1** The titration curves of a strong acid (e.g. HCl) added either to a strong base (e.g. NaOH) or to a weak base (e.g.  $\text{NH}_3$ ).



**Figure 2** The titration curves of a strong base (e.g. NaOH) added either to a strong acid (e.g. HCl) or to a weak acid (e.g.  $\text{CH}_3\text{COOH}$ ).

The equivalence point, or stoichiometric point, corresponds to the mixing together of stoichiometrically equivalent amounts of acid and base. Note that the pH at equivalence is not necessarily 7 (see table 1 below):

- The pH of a weak base at the end-point (equivalence) lies below pH 7.  
At equivalence, the solution contains the salt of a weak base: this is an acid (the conjugate acid of the weak base) and so the solution is acidic.
- The pH of a weak acid at the end-point (equivalence) lies above pH 7.  
At equivalence, the solution contains the salt of a weak acid: this is a base (the conjugate base of the weak acid) and so the solution is basic.

Figure	system	pH at start	pH at equivalence	pH at twice equivalence
1	strong base + strong acid	13.0	7.0	1.5
1	weak base + strong acid	<13.0	<7.0	1.5
2	strong acid + strong base	1.0	7.0	12.5
2	weak acid + strong base	>1.0	>7.0	12.5

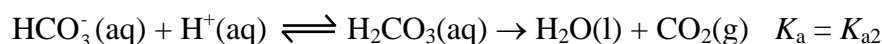
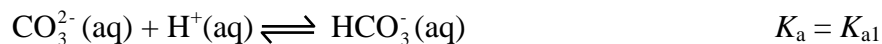
**Table 1** The pH at the start, equivalence and twice equivalence for various combinations of acids as shown in the titration curves in figures 1 and 2.

If a weak acid is added to a weak base, the variation of pH with volume near to the end-point is too gradual for the equivalence point to be detected easily (see figure 3 below left). There are titrations in which more than one equivalence point can occur. Two such titrations are discussed below.

### 1. Titrating sodium carbonate with hydrochloric acid

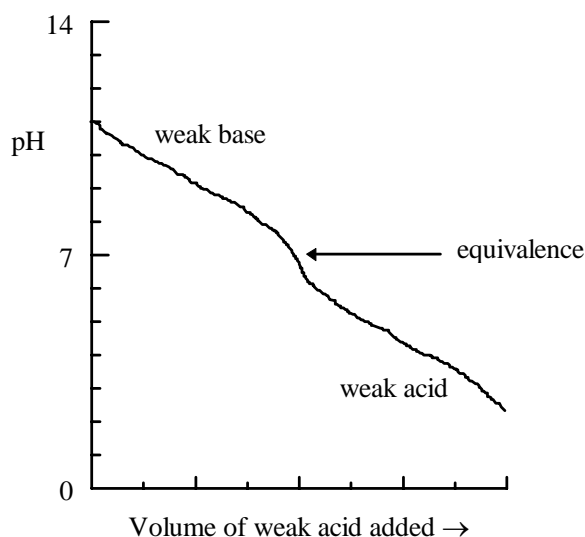
The carbonate ion,  $\text{CO}_3^{2-}$ , is the conjugate base of the carbonic acid,  $\text{H}_2\text{CO}_3$ , a weak acid. It acts as two successive Brønsted-Lowry bases, and so will accept two protons from a Brønsted-Lowry acid.

The two proton-accepting equilibria are:

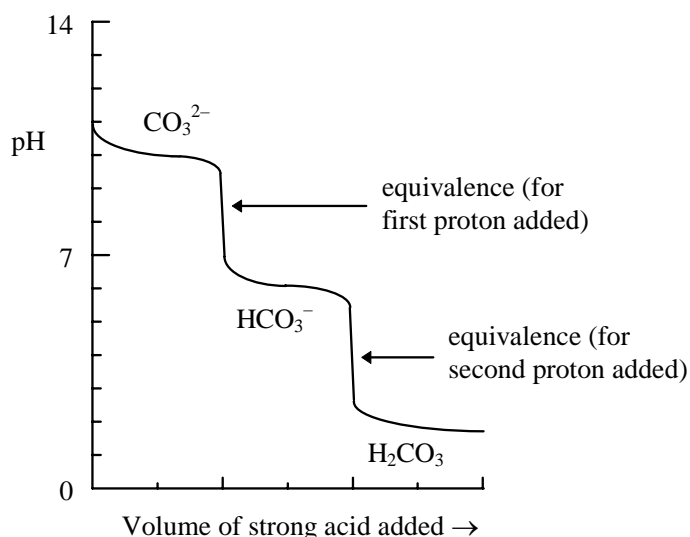


(Note: the acid dissociation constants,  $K_a$ , refer to the proton loss reactions, i.e. the reverse of the equilibria as written).

When sodium carbonate is titrated with a strong acid, the titration curve has **two** equivalence points. These correspond to the adding of each successive proton to the base, and occur at pH 8.31 and pH 3.69 (see figure 4 below right).



**Figure 3** The titration curve of a weak acid added to a weak base.

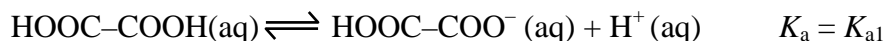


**Figure 4** The titration of sodium carbonate with hydrochloric acid.

### 2. Titrating ethanedioic acid with sodium hydroxide

Ethanedioic acid (also known as oxalic acid – found in rhubarb) is a diprotic acid. It acts as two successive Brønsted-Lowry acids, and so will donate two protons to a Brønsted-Lowry base.

The two proton-donating equilibria are:



The first proton is removed from a neutral molecule, but the second proton is removed from a negatively charged ion. This means that the second proton is more difficult to remove than the first, and so  $\text{p}K_{a2} > \text{p}K_{a1}$ . In fact,  $\text{p}K_{a1} = 1.23$  and  $\text{p}K_{a2} = 4.19$ , and so both acids are also weak acids.

When ethanedioic acid is titrated with a strong base, the titration curve has **two** equivalence points. These correspond to the removal of each successive proton from the acid, and occur at pH 2.71 and pH 8.36 (see figure 5 right).

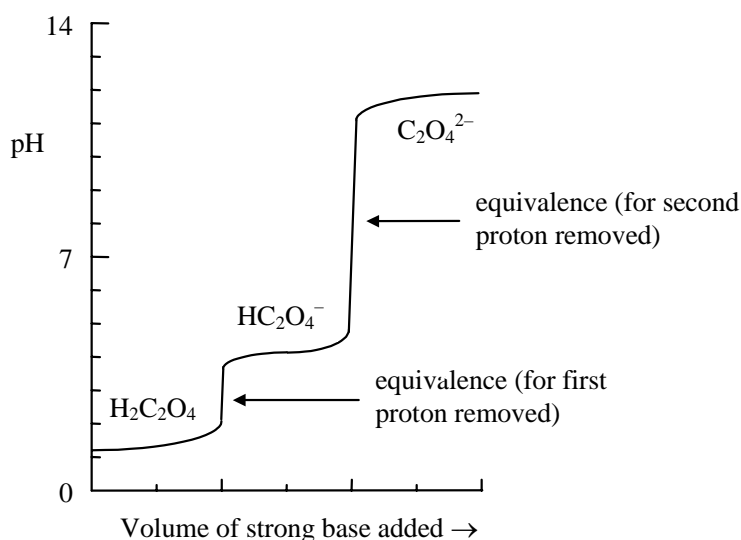
### Indicators

Acid-base indicators are water-soluble weak organic acids. Their acid and base forms have different and intense colours, and there is an equilibrium between the two forms:



acid form                  base form

colour 1                  colour 2



**Figure 5** The titration of ethanedioic acid with sodium hydroxide solution.

At the end-point of an acid-base titration the pH changes very rapidly, and the indicator equilibrium moves from **all** HInd to **all** Ind<sup>−</sup> (or *vice versa*). This means that if a few drops of indicator solution have been added, there is also a colour change from colour 1 to colour 2 (or *vice versa*). At low pH when there are a lot of H<sup>+</sup> ions, the main species is the undissociated acid HInd, so you see colour 1. At high pH, the main species is the conjugate base Ind<sup>−</sup>, so you see colour 2. The colour changes over a *range* of pH, however, and this range is different for each indicator (see table 2 below).

indicator	colour 1 – acid HInd	pH range	colour 2 – base Ind <sup>−</sup>
methyl orange	red	3.2 to 4.4	yellow
phenolphthalein	colourless	8.2 to 10.0	pink

**Table 2** Characteristics of two common indicators. Note that methyl orange has an unusually narrow pH range compared to most other indicators.

It is important to choose the correct indicator for the job, so watch out for examination questions that test your understanding of this. An indicator is appropriate for a given titration if the rapid change of pH at equivalence overlaps the pH range of the indicator. Table 3 (below) summarises some titrations and the choice of appropriate indicators for them.

acid	base	pH change	choice of indicator
HCl	NaOH	3 to 11	methyl orange or phenolphthalein – the pH change here is over a very wide range
HCl	NH <sub>3</sub>	3 to 7	methyl orange
CH <sub>3</sub> COOH	NaOH	7 to 11	phenolphthalein
CH <sub>3</sub> COOH	NH <sub>3</sub>	no sharp change	no suitable indicator – a pH meter is not suitable either as there are no sudden pH changes
HCl	Na <sub>2</sub> CO <sub>3</sub>	6.5 to 9.5 (pK <sub>a1</sub> ) 2.5 to 5.5 (pK <sub>a2</sub> )	phenolphthalein for pK <sub>a1</sub> methyl orange for pK <sub>a2</sub>
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	NaOH	1.5 to 3.5 (pK <sub>a1</sub> ) 5 to 11 (pK <sub>a2</sub> )	methyl orange for pK <sub>a1</sub> phenolphthalein for pK <sub>a2</sub> (the first pH change only just falls within the range of methyl orange, so a pH meter more suitable here)